U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-257 691

Radioactivity Distribution in Phosphate Products, By-Products, Effluents, and Wastes

Office of Radiation Programs

Aug 75

271068

PB 257 691
TECHNICAL NOTE
ORP/CSD-75-3

RADIOACTIVITY DISTRIBUTION IN PHOSPHATE PRODUCTS, BY-PRODUCTS, EFFLUENTS, AND WASTES

REPRODUCED BY
NATIONAL TECHNICAL
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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

THE UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RADIATION PROGRAMS

AUGUST 1975

BIBLIOGRAPHIC DATA SHEET	1. Report No. ORP/CSD-75-3	2.	3. Recipient's Accession No. PB-257 691
4. Title and Subtitle Radioactivity Distribution in Phosphate Products, By-Products, Effluents, and Wastes			5. Report Date Aug 75 6.
7. Author(s) Richard J. Guimond, and Samuel T. Windham			8. Performing Organization Rept. No.
9. Performing Organization Name and Address Office of Radiation Programs, Washington, D.C. Div. of Criteria and Standards			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Organization Name and Address			13. Type of Report & Period Covered 14.

15. Supplementary Notes

16. Abstracts

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17. Key Words and Document Analysis. 17a. Descriptors

*Phosphate deposits,
*Radioactive materials,
*Radiation hazards,
*Radioactive contaminants,

Uranium,
Thorium,
Ore sampling,
Radioactive wastes,
Phosphoric acids,
Industrial plants,
Fertilizers,
By-products.

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 13 B 18 H

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
National Technical Information Service Springfield, Virginia 22161	UNCLASSIFIED	41p
	20. Security Class (This Page) UNCLASSIFIED	22. Price 4.00/2.25

FORM NTIS-35 (REV. 10-73) ENDORSED BY ANSI AND UNESCO. THIS FORM MAY BE REPRODUCED USCOMM-DC 8265-P74

Technical Note
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RADIOACTIVITY DISTRIBUTION IN PHOSPHATE PRODUCTS, BY-PRODUCTS, EFFLUENTS, AND WASTES

by

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August 1975

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PREFACE

The Office of Radiation Programs of the Environmental Protection Agency carries out a national program designed to evaluate population exposure to ionizing and non-ionizing radiation, and to promote development of controls necessary to protect the public health and safety. This report was prepared in order to determine the natural radioactivity source terms associated with phosphate mining and milling products, by-products, effluents, and wastes. Readers of this report are encouraged to inform the Office of Radiation Programs of any omissions or errors. Comments or requests for further information are also invited.

William A. Mills

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ABSTRACT

Phosphate rock throughout the world contains uranium in concentrations ranging from a few ppm to a few hundred ppm. In the United States, phosphate rock normally contains between 100-150 ppm uranium. Mining and processing of these ores redistributes much of the uranium daughters among the various products, by-products, and wastes. These materials are then widely dispersed throughout the environment. This redistribution may lead to increased exposure of the public to these naturally-occurring radionuclides. In determining the magnitude of the population exposure caused by this redistribution and in developing environmental standards and controls to prevent contamination of the biosphere from these naturally-occurring radionuclides it is necessary to determine the concentrations and total quantities of these radionuclides in the products, by-products, effluents and wastes of phosphate mining and manufacturing.

Samples of phosphate ores, products, by-products, effluents, and wastes were obtained and analyzed for their radioactivity content. Calculations were made to quantify the partitioning of the radionuclides in the processing steps from mining through the wet and thermal production techniques. Laboratory studies were made to establish the effectiveness of various treatments in controlling radioactivity in liquid effluents. Field studies were conducted to verify the laboratory results and assess liquid effluent control effectiveness in actual facility operations. Quantities of radioactivity entering the environment through various products, by-products, effluents, and wastes were estimated.

Presented at the Session on Disposal and Utilization of Wastes from Phosphate Fertilizer Production, 1975 American Chemical Society Annual Meeting, Chicago, Illinois, August 24-29, 1975.

INTRODUCTION

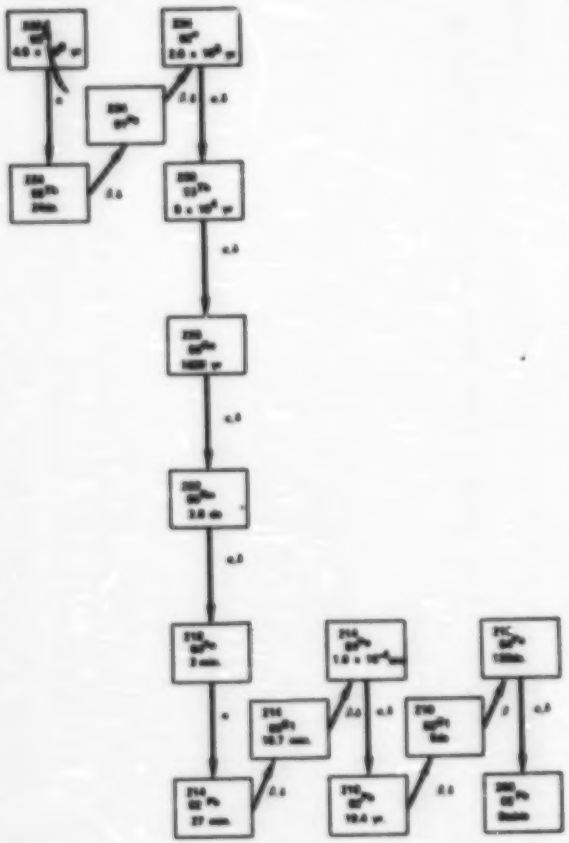
It has been recognized for several years that phosphate deposits throughout the world contain appreciable concentrations of radioactive material originating from the decay of uranium and thorium present in the ores. Previous studies of the variability of concentrations of natural uranium and thorium in the phosphate ores produced in the United States indicate that they range from 8 to 399ppm (5.4 to 267 pCi per gram) and 2 to 19 ppm (0.4 to 4 pCi per gram), respectively (1). The highest concentrations were reported in South Carolina phosphate and the lowest were in Tennessee phosphate rocks.

Generally, the uranium daughters in the ores, at least through radium-226, have been shown to be in secular equilibrium. This means that for each curie (3.7×10^{10} disintegrations/sec) of the parent radionuclide, such as uranium-238, there is one curie of each daughter radionuclide also present. Figures 1, 2, and 3 illustrate the uranium, actinium, and thorium decay series. From the figures it is readily observed that uranium-238, uranium-234, thorium-230, and radium-226 all belong to the uranium series; uranium-235 and thorium-227 are in the actinium series; and thorium-232 and thorium-228 are members of the thorium series. Consequently, when in secular equilibrium, members of the same series will display equal activity.

Mining and processing phosphate ores redistributes the uranium, thorium, and their decay products among the various products, by-products, and wastes. As a result of dispersal of the materials throughout the environment, there may be increased exposure to the public

FIGURE 1

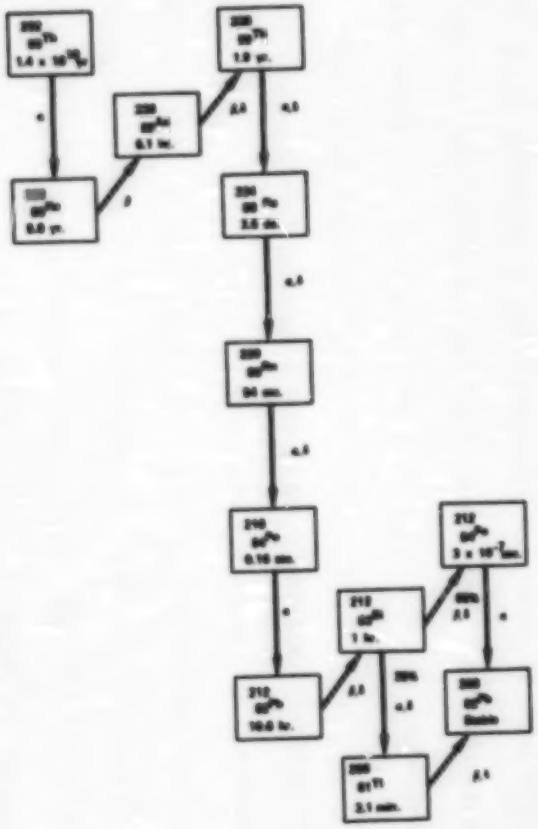
URANIUM - 238 DECAY SERIES



1A

FIGURE 2

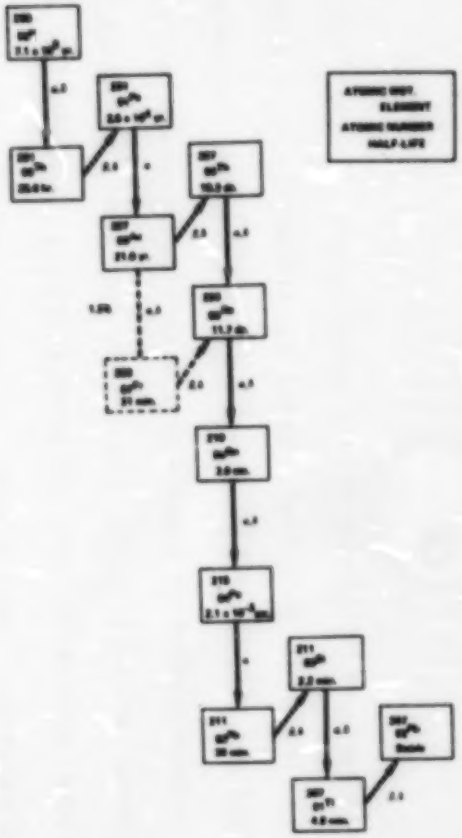
THORIUM - 232 DECAY SERIES



1B

FIGURE 3

ACTINIUM (URANIUM-235) DECAY SERIES



1C

from these naturally-occurring radionuclides. Although some scientific work has been performed regarding radioactivity in phosphate related materials, the quantitative aspects have generally focused on determining the concentration of uranium in the various phosphate formations. These efforts have primarily been undertaken from a geological perspective. Little emphasis has been placed on the health physics or environmental radioactivity perspectives of the various industry operations. Therefore, in order to evaluate the population dose from phosphate materials and thus determine the adequacy of present standards and environmental controls, it was necessary to first quantitate the radioactivity source terms from the individual operations. This was done by analytically determining the concentrations in specific products, by-products, effluents and wastes and estimating the total activity of the various radionuclides that may be entering the environment through different materials. Establishing the concentrations in specific products, process waters, wastes, and by-products enable the estimating of local and regional impacts while estimates of total activity from annual production data will enable evaluation of national impacts as well as comparision with other industries that release natural radionuclides to the environment.

METHODOLOGY

Samples of phosphate ores, products, by-products, effluents, and wastes were obtained from several mines, wet process phosphoric acid plants, and electric furnace facilities throughout the southern United States and analyzed for their uranium, radium-226, and thorium content. Laboratory studies were made to determine the effectiveness of various neutralization treatments in controlling radioactivity in liquid effluents from wet-process phosphoric acid plants. Field studies were conducted at several wet-process phosphoric acid plants to verify the results of the laboratory studies.

Radium-226 analyses were performed using the radon emanation method as described in the American Public Health Association's Methods for the Examination of Water and Waste Water (2). By this method, the radium was chemically separated from the samples using a barium sulfate precipitation. It was then dissolved in acid and stored in sealed glass tubing for three weeks to allow ingrowth of radon-222, the gaseous daughter of radium-226. The radon gas was then emanated into an evacuated zinc coated chamber and counted for alpha activity.

Uranium and thorium were separated from solubilized samples using liquid ion exchange procedures developed at the Environmental Protection Agency's Eastern Environmental Radiation Facility in Montgomery, Alabama. Samples were then coprecipitated and collected on a 0.2 micron pore filter and counted by alpha spectroscopy using solid state surface barrier detectors.

PHOSPHATE ROCK MINING AND BENEFICIATION

Uranium was once thought to be very scarce, yet now it is considered to be more plentiful than many other elements including mercury, antimony, silver, and cadmium (3). It occurs in numerous minerals and ores including pitchblende, uranite, caronite, autunite, uranophane, lignite, monazite sands, and phosphate rock. Naturally-occurring uranium contains 99.28% uranium-238, 0.71% uranium-235, and 0.0058% uranium-234 (4).

Thorium is believed to be more plentiful than uranium. It occurs naturally as thorium-232. Natural thorium is frequently associated with uranium in mineral deposits. Commercial production of thorium in the United States has usually been from monazite sands.

Although uranium is present in most phosphate deposits, the higher concentrations are associated with the marine phosphate deposits (5). This is probably due to the dissolution of the uranium by the marine environment and later redeposition (6). Marine deposits comprise all of the phosphate materials presently extracted in the United States. In Florida, uranium is substituted for calcium in the extensive phosphate deposits.

All of the analytical results from the field studies have not been obtained. Table 1 presents the results of the analytical determinations for radium-226, uranium, and thorium concentrations in Florida phosphate mine products and wastes. The data indicates that in all of the mine materials, the radionuclides of uranium and actinum decay series are in equilibrium. The members of the thorium series are quite close to

TABLE 1

RADIUM-226, URANIUM AND THORIUM CONCENTRATIONS IN FLORIDA PHOSPHATE MINE PRODUCTS AND WASTES

MATERIAL	RADIUM – 226 (pCi/GRAM)	URANIUM (pCi/GRAM)			THORIUM (pCi/GRAM)			
		234	235	238	227	228	230	232
MARKETABLE ROCK	42	41	1.9	41	2.0	0.61	42.3	0.44
SLIMES	46	42	2.8	44	2.3	1.2	48	1.4
SAND TAILINGS	7.5	5.2	0.38	5.3				

equilibrium. The low activity of the thorium-232 and thorium-228, particularly in the marketable rock samples, cause an error term of about ± 30 percent in the analyses so they may be in true equilibrium. These findings both confirm previous examinations of phosphate rock and shows that the primarily physical separations of beneficiation do not significantly alter the states of equilibrium, although beneficiation does produce a redistribution of the concentrations of the radionuclides from the mine rock to the marketable rock, slimes, and sand tailings.

With respect to concentration, the marketable rock and slime contain more radium-226, uranium and thorium than does the sand tailings. This

is expected because the radioactivity is directly associated with the phosphate compound structure, and the marketable ore and slimes contain most of phosphate. One-third of the phosphate originally contained in the matrix remains in the slimes (7). The remainder is primarily in the marketable rock.

In order to estimate the total annual radium-226, uranium, and thorium activities extracted by phosphate mining, the production data from 1973 was examined. In that year, 91% of the overall mine rock production came from Florida, 3% from Tennessee, and the remainder from the Western states of Idaho, Missouri, Montana, Utah, and Wyoming (8). Eighty-two percent of the marketable rock produced was from Florida, 6% was from Tennessee, and the remainder was from the Western states. Over 99.9% of the mine production in Florida was beneficiated, whereas, about 59% of the Western mine production was beneficiated. While estimates of sand tailings and slime production indicate that they vary from mine to mine, there are approximately 3250 pounds of sand tailings and 2110 pounds of slimes produced per ton of marketable rock (9). Clearly, with 1973 marketable rock production of 42.1 million tons, a sizable quantity of slimes and sand tailings were produced.

Field investigations and sample analyses for Tennessee and Western mine materials have not been completed. Therefore, estimates of the total amounts of radium-226, uranium, and thorium extracted in phosphate mining are only for Florida. It is believed that this probably underestimates the total amounts of radioactivity extracted by about 10 to 15 percent since Tennessee rock should contain relatively low

TABLE 2

ESTIMATED TOTAL RADIUM-226, URANIUM, AND THORIUM ACTIVITIES IN FLORIDA PHOSPHATE MINE PRODUCTS AND WASTES

MATERIAL	1973 PRODUCTION ($\times 10^6$ TONS)	RADIUM – 226 (CURIES)	URANIUM (CURIES)			THORIUM (CURIES)			
			234	235	238	227	228	230	232
MINE ROCK	127.3								
MARKETABLE ROCK	34.4	1200	1200	58	1200	62	19	1220	14
SLIMES[a]	36.3	1400	1300	66	1400	74	30	1570	48
SAND TAILINGS[b]	65.8	260	264	19	260				
TOTAL	128.5	3160	2844	164	2920				

(a) Based on 2110 pounds of slimes produced per ton of product
(b) Based on 3320 pounds of sand tailings produced per ton of product

radioactivity concentrations and Western rock concentrations should be comparable to Florida rock. Table 2 lists the estimated total quantities of products and wastes from Florida phosphate mining in 1973 and estimates the total activities of radium-226, uranium and thorium present in the materials based on the concentrations in Table 1. Blanks in the table indicate that specific estimates for that parameter have not been made because of incomplete sample analyses. Of the total radioactivity present in the 1973 total beneficiation plant products and wastes, approximately 40% was in the marketable rock, 48% was in the slimes, and the remainder was in the sand tailings.

Several slime ponds have discharges to the environment. The discharge quantities depend upon the facility's degree of recycle, overall water consumption and, local precipitation. Since most of the radioactivity in the waste products of beneficiation is present in the slimes, this could pose potential problems to receiving streams if the radioactivity was not removed prior to discharge. To examine this aspect, the concentration of radium-226 was determined for slime discharges and effluent discharges from seven mine and beneficiation plants. This data is illustrated in Table 3. The concentration of dissolved radium-226 in slime discharges is less than 5.0 picocuries per liter at all seven facilities. The concentration of radium-226 in the undissolved fraction varies greatly and is highly dependent on the total suspended solids in the slime discharge. The radium-226 concentrations in picocuries per gram of the undissolved fraction at all seven facilities are in the same order of magnitude emphasizing the importance of the total suspended solids concentration in determining the total concentration of radium-226 in picocuries per liter in the slime discharge. Although no chemical process is used to treat the discharge from the slime ponds, low dissolved radium-226 concentrations were observed in the effluents. This is attributed to the generally low dissolved radium-226 concentrations in the slime discharges.

The total concentration of radium-226 in every effluent discharge sample analyzed was less than 3.0 picocuries per liter. Comparison of the slime discharge and effluent discharge concentrations indicate that no specific reduction in soluble radium-226 is predictable from the data

TABLE 3

RADIUM-226 CONCENTRATIONS IN PHOSPHATE MINE EFFLUENTS

FACILITY	HEAVY SLIME DISCHARGE			EFFLUENT DISCHARGE			
	DISSOLVED	UNDISSOLVED		DISCHARGE POINT	DISSOLVED	UNDISSOLVED	
	pCi/LITER	pCi/LITER	pCi/gm		pCi/LITER	pCi/LITER	pCi/gm
1	0.82	10.2	21.3	A	0.66	0.26	17.3
				B	0.52	0.29	21.5
				C	0.68	0.28	18.7
2	4.8	1074	72.6	A	0.02	0.56	31.1
					0.34	1.1	52.4
3	2.0	97.6	30.5	A	2.2	0.74	38.9
4	0.6	37.7	9.8	A	0.24	0.74	28.5
5	2.2	520	52.0	–	–	–	–
6	1	2248	33.6	–	–	–	–
7	0.56	725.5	15.0	A	1.01	0.14	7.0

obtained at the seven facilities. This is understandable since present treatment of the slimes involves only settling of solids and consequently no appreciable precipitation of soluble radium-226 would be expected. The reduction of total radium-226 from the slime discharge to the effluent discharge ranged from 92% to greater than 99.9% in the facilities studied. This was primarily due to removal of suspended solids containing large amounts of radium-226. Therefore, because of the

significance of the contribution of the radium-226 contained in the suspended solids to the total concentration of radium-226 observed in either the slime or effluent discharge, great reductions in suspended solids levels between the slime discharge and the effluent will result in corresponding reductions in radium-226 concentrations.

WET-PROCESS PHOSPHORIC ACID PRODUCTION

With 1973 production of 5.62 million tons P_2O_5 of phosphoric acid, that year about 20 million tons of marketable rock went to the production of phosphoric acid by the wet process method. Under the provisions of the Federal Water Pollution Control Act of 1972, as amended, the Environmental Protection Agency is required to establish effluent limitation guidelines for fertilizer and phosphate manufacturing and to issue National Pollutant Discharge Elimination System (NPDES) permits for individual fertilizer and manufacturing facilities. Because of the need to expeditiously issue permits to such facilities, interim guidelines for permits recommended a effluent limitation of 9 pCi per liter total radium-226 pending results from additional studies (10). To provide a data base for subsequent guidelines and permits, laboratory studies were conducted to investigate the reduction in radium-226 levels after various treatments. Process pond water was obtained from a Florida wet-process facility. Four bases, quick lime, limestone, hydrated lime, and dolomite were added to 4 liters of process water in different amounts to increase the pH. Other bases such as sodium hydroxide were not studied because they did not appear to be economically viable treatment alternatives if the bases studied proved satisfactory. After the bases were added, they were vigorously agitated and allowed to settle until the pH stabilized. The resultant supernatant liquids were then filtered and analyzed for their soluble radium-226 concentrations. No attempt was made to examine the undissolved radium-226 concentrations because the

TABLE 4

LABORATORY PROCESS WATER TREATMENT STUDY

TREATMENT	AMOUNT OF BASE ADDED (GRAMS)	RESULTANT pH	DISSOLVED RADIUM - 226 pCi/LITER
UNTREATED PROCESS WATER	-	2.0	76.8 (8.7 pCi/LITER UNDISSOLVED)
CALCIUM OXIDE (QUICK LIME)	70	7.9	0.15
LIMESTONE ROCK	500	4.8	0.11
SLAKED LIME (HYDRATED LIME)	50	8.0	0.07
DOLOMITE	500	4.0	0.16

differences between laboratory settling and field settling of solids were deemed to be significant enough to make the laboratory undissolved radium fraction not representative of the field situation. The results of these studies are detailed in Table 4. In all treatment cases, soluble radium-226 was reduced by more than 99.7%. This was true even though the resultant pH of the treated wastes ranged from 4.0 to 8.0. This large reduction is attributed to the readily available amount of sulfate ions

TABLE 5
EFFECT OF LIME TREATMENT ON RADIOACTIVITY REMOVAL FROM EFFLUENTS FROM A WET PROCESS PHOSPHORIC ACID PLANT

PLANT A – FIELD SURVEY NUMBER 1

SAMPLE I.D.	pH	TOTAL RADIUM - 226(pCi/l)	TOTAL URANIUM (pCi/l)			TOTAL THORIUM (pCi/l)		
			234	235	238	230	229	232
UNTREATED PROCESS WATER	2.0	62.3	1055	48	1065	2.5	70	4.5
OUTFALL (After double liming)	9.1	4.84	1.69	ND	0.52	0.44	0.57	0.04

PLANT A – FIELD SURVEY NUMBER 2

SAMPLE I.D.	pH	TOTAL RADIUM - 226 (pCi/l)	TOTAL URANIUM (pCi/l)			TOTAL THORIUM (pCi/l)		
			234	235	238	230	229	232
UNTREATED PROCESS WATER	1.5	55.0	411	34	384	3.4	101	3.2
LIMED ONCE	4.4	1.39						
PRIOR TO SECOND LIMING	4.3	1.5	36.7	2.2	35.5	ND	0.02	ND
OUTFALL (After second liming)	7.1	1.0	16.0	0.99	16.0	0.32	0.71	0.11

in the process water enabling large scale coprecipitation of calcium-radium sulfate.

Field studies were conducted at several wet-process facilities to verify the effectiveness of lime treatment as observed in the laboratory. Results of four of these studies are detailed in Tables 5, 6, and 7. Field studies were conducted at Plant A during different periods of the

TABLE 6

EFFECT OF LIME TREATMENT ON RADIOACTIVITY REMOVAL FROM EFFLUENTS FROM A WET PROCESS PHOSPHORIC ACID PLANT/PLANT B - FIELD SURVEY NUMBER 1

SAMPLE I.D.	pH	TOTAL RADIUM - 226 (pCi/l)	TOTAL URANIUM (pCi/l)			TOTAL THORIUM (pCi/l)		
			234	235	238	228	230	232
UNTREATED PROCESS WATER*	2	88.2	1760	88.8	1630	3.62	360	6.33
AFTER FIRST* LIMING	4.5	74.0	730	33.4	730	6.15	4.3	7.5
PRIOR TO SECOND LIMING	6	0.89	67.8	3.17	65.1	ND	1.32	ND
OUTFALL (After double-liming)	8	0.45	0.26	ND	0.33	0.1	0.13	ND
UNTREATED NON-PROCESS WATER		1.20	0.39	ND	0.39	ND	ND	ND
NON-PROCESS WATER AFTER LIMING		2.8	0.95	ND	0.75	0.13	0.79	0.87
NON-PROCESS WATER OUT-FALL		0.89	0.34	ND	0.42	ND	1.32	ND

*These concentrations are high because of the large suspended solids load of 23.5 grams per liter.

The dissolved concentrations in pico curies per liter were:

Radium - 226 - 6.2
Uranium - 234 - 13.5
Uranium - 235 - 0.62
Uranium - 238 - 12.9

TABLE 7

EFFECT OF LIME TREATMENT ON RADIOACTIVITY REMOVAL FROM EFFLUENTS FROM A WET PROCESS PHOSPHORIC ACID PLANT

PLANT C - FIELD SURVEY NUMBER 1

SAMPLE I.D.	pH	TOTAL RADIUM - 226 (pCi/l)	TOTAL URANIUM (pCi/l)			TOTAL THORIUM (pCi/l)		
			234	235	238	228	230	232
PROCESS WATER	1.9	65.2	676	26.1	661	0.66	0.8	4.1
OUTFALL (After single liming)	6.8	2.65	.26	ND	.28	ND	ND	ND

rainy season. Field survey number 1 was conducted very early in the rainy season, prior to the initiation of large scale effluent treatment. Field survey number 2 was performed late in the rainy season after almost continuous lime treatment for over two months.

From Table 5, comparison of the process water from survey number 1 to survey number 2 shows a 32% decrease in radium-226 concentration during the second survey. This is probably due to the combination of dilution of the process water by the influx of surface rain runoff and the removal of the radioactive material by treatment and discharge of several million gallons of water per day.

The data indicate that the radionuclides are substantially out of equilibrium. This is because the uranium, and thorium are dissolved preferentially over radium-226 by the acidulation with sulfuric acid and then enter the process water. In all four process water samples, the uranium activity was a factor of 10 or more greater than the radium-226 activity. The thorium-230 activity varied greatly, ranging from .2 to 4.5 times the radium-226 activity.

As evidenced by Tables 5, 6, and 7, treatment with lime is highly efficient in removing radium-226 from the discharged process water. In all four cases, the outfall samples exhibited radium-226 reduction of greater than 94 percent. This data argrees very well with removal efficiencies observed in laboratory experiments. Lime treatment also proved to be extremely effective in removing uranium and thorium-230 from treated process water. In addition, uranium and thorium-230 removal between the process water and outfall were at least 96 and 99 percent, respectively in the four cases noted.

Therefore, although primarily designed for pH, phosphorus and flourides control and not for removal of radionuclides in the effluent, treatment with lime was observed to be highly effective in removing

radium-226, uranium, and thorium from the effluent discharge. These results are attributed to the following factors:

1. Process water contains a large concentration of sulfate and phosphate ions to enable ready compound formation.

2. Neutralization by an agent such as lime not only allows for the reduction of solubility of several compounds but provides an ample supply of calcium ions to enable the large-scale formation of calcium sulfate.

3. The relative insolubility of radium sulfate makes its readily coprecipitate with calcium sulfate.

4. Uranium and thorium probably precipitate along with calcium sulfate and other components through substitution for calcium in formed compounds. Information Circular 8501, U.S. Department of the Interior, Bureau of Mines, 1971.

5. Settling provides the opportunity for the precipitated compounds to be removed from the effluent and not be discharged as suspended solids.

Samples of normal superphosphate, diammonium phosphate (DAP) monoammonium phosphate (MAP), triple superphosphate (TSP), phosphoric acid, animal feed supplement, sodium fluosilicate, and gypsum were obtained from several facilities using Florida phosphate rock. Radium-226, uranium, and thorium data for these samples are shown in Table 8. The uranium and thorium analyses for these samples are not all completed. For the samples completed there is significant disequilibrium between uranium-238, thorium-230, and radium-226. Although results are not available, the normal superphosphate samples probably exhibit equilibrium

TABLE 8

RADIUM-226, URANIUM, AND THORIUM CONCENTRATIONS IN WET PROCESS PHOSPHORIC ACID PLANT PRODUCTS AND BYPRODUCTS*

MATERIAL	RADIUM - 226 (pCi/gm)	URANIUM (pCi/gm)			THORIUM (pCi/gm)			
		234	235	238	227	228	230	232
GYPSUM	33	6.2	0.32	6.0	0.97	1.4	13	0.27
NORMAL SUPER-PHOSPHATE	25							
DIAMMONIUM PHOSPHATE (DAP)	5.6	63	3.0	63	1.6	0.8	65	0.4
TRIPLE SUPER-PHOSPHATE (TSP)	21	58	2.8	58	1.2	0.9	48	1.3
MONOAMMONIUM PHOSPHATE (MAP)	5.0	55	2.9	55				
SODIUM FLOUROSILICATE	0.28							
ANIMAL FEED	5.5							
PHOSPHORIC ACID	840 pCi/l							

*PLANTS USING FLORIDA PHOSPHATE ROCK

because the production of normal superphosphate does not require the separation of gypsum from the reaction products.

Gross mass balancing of the input phosphate rock and the product phosphoric acid and phosphogypsum indicates that approximately 1 percent of the radium-226, 60 to 80 percent of the thorium-230, and 80 percent of the uranium is dissolved during the acidulating by sulfuric acid. The thorium-230 fraction appears to be the most variable. The numbers are

quite similar to radium-226, uranium, and thorium dissolution by the acid leach process of milling uranium ore (11). This is not surprising since similar techniques and chemicals are used in both industrial processes.

Individual samples of phosphoric acid displayed a great variation of radium-226 concentration ranging from a few hundred to greater than one thousand picocuries per liter. The variation was not observed to be a function of solids content or P_2O_5 concentration. The average of seven samples was 840 pCi/liter as noted in the table. This translates to a concentration of less than 1 pCi per gram of 52% phosphoric acid.

Ammonium phosphates (DAP and MAP) were observed to have approximately the same radium-226 concentrations. Uranium concentrations were greater by a factor of about ten, although the DAP had slightly higher uranium concentrations than the MAP. The relatively low radium-226 concentration and much higher uranium concentration is attributed to the fact that production of ammonium phosphates uses only ammonia and phosphoric acid with no direct reaction with phosphate rock. Consequently, the bulk of the radioactivity introduced to the reaction comes from the phosphoric acid which is enriched with uranium and deficient in radium-226 due to the partition by removal of the phosphogypsum. Thorium-230 concentrations were about the same as the uranium concentrations which is expected because of their similarity in dissolution fractions.

Triple superphosphate (TSP) contained almost as much radium-226 as normal superphosphate fertilizer and if we assume normal superphosphate

TABLE 9

ESTIMATED TOTAL RADIUM-226 URANIUM, AND THORIUM ACTIVITY IN PHOSPHATE FERTILIZER PRODUCTS AND BYPRODUCTS BASED ON 1973 PRODUCTION DATA[a]

MATERIAL	PRODUCTION		RADIUM - 226 (CURIES)	URANIUM (CURIES)			THORIUM (CURIES)			
	(x 10^6 TONS)	(x 10^6 TON P_2O_5)		234	235	238	227	228	230	232
NORMAL SUPER-PHOSPHATE	3.4	0.82	77							
TRIPLE SUPER-PHOSPHATE	3.7	1.72	89	180	9.4	180	4	3.8	160	1.3
AMMONIUM PHOSPHATES	5.3	2.87	30	330	16	330	8.4	4.2	340	2.1
PHOSPHERIC ACID	11[c]	5.82	8.5				—			
GYPSUM[b]	28.3	–	700	140	7.3	140	22	32	280	6.2

(a) Wet Process Production
(b) Based on 4.5 tons gypsum per ton P_2O_5
(c) Assuming 69 percent P_2O_5 acid

fertilizer is in equilibrium, TSP probably contains more than twice the concentration of uranium than normal superphosphate. These observations are in accord with anticipated results because triple superphosphate is produced by acidulating phosphate rock with phosphoric acid. Therefore, the product triple superphosphate would be expected to display comprise activities of radium-226, uranium, and thorium corresponding to the activities in the reactants, phosphate rock and phosphoric acid, which display markedly different radium-226, uranium, and thorium concentrations.

The other two product samples studied were animal feed supplement which contained about the same radium-226 concentration as the ammonium phosphate samples, and sodium fluosilicate which contained very little radium-226. The low radium-226 in the sodium fluosilicate infers that by-product fluosilicic acid which is used to produce the sodium fluosilicate also contains very little radium-226. Uranium and thorium analyses have not yet been obtained for these two products.

In order to estimate the total activities of radium-226, uranium, and thorium in the wet phosphoric acid plant products, and by-products, 1973 production data was obtained and used in conjunction with the product radioactivity concentrations detailed in table 8 (12). The resulting total activity estimates are illustrated in table 9. Blanks reflect that no estimates were made because of incomplete data. It should be noted that because of the difficulty in separating production on the basis of Florida rock versus Western rock, all total estimates assume that products made with Western rock exhibit approximately the same radioactivity concentrations. Although this assumption may not be completely valid, it is anticipated that the error introduced into the estimates is within the error built into the production estimates and product radioactivity concentrations.

Approximately 80% of the product radium-226 activity is contained in the phosphogypsum. Although the radium-226 concentrations of normal superphosphate and triple superphosphate are about 70% of the phosphogypsum, the bulk magnitude of the amount of phosphogypsum produced, about 4.5 tons per ton P_2O_5 acid, is sufficient to outweigh the

individual contributions of the other products (13). Phosphoric acid contributes a major portion of the total uranium and thorium activity. It is emphasized that the columns are not directly additive to determine the total radioactivity in the products because some of the activity reflected in the phosphoric acid is also accounted in the ammonium phosphate and triple superphosphate estimates because phosphoric acid is used to produce these products. Nevertheless, it is evident that a sizable inventory of radioactivity is present in the phosphoric acid plant products and by-products.

ELEMENTAL PHOSPHORUS PRODUCTION

Three elemental phosphorus plants were studied, one using a blend of Florida and Tennessee rock, and two others using only Florida rock. The results of radium-226 analysis of the raw materials and products of these facilities are shown in Tables 10 and 11.

Because of the hazards associated with handling elemental phosphorus, special procedures had to be established to analyze it for radioactivity. Consequently, the early field trips omitted phosphorus samples until appropriate analytical measures were established and analytical results of their radium-226 content are not available. However, elemental phosphorus samples have been obtained during subsequent field trips to the two facilities using only Florida rock. Of all the raw materials used in the production of elemental phosphorus, only the phosphate rock and particularly the Florida rock show significantly elevated radium-226 concentrations. The slag exhibits the greatest concentration of radioactivity of the solid products. In a mass balance of radium-226 entering and leaving these elemental phosphorus plants, almost all of it can be accounted for in the input phosphate rock and in the output slag.

TABLE 10

RADIUM-226 CONCENTRATIONS IN ELEMENTAL PHOSPHORUS PLANT RAW MATERIALS, PRODUCTS, AND BYPRODUCTS

AVERAGE OF TWO PLANTS USING FLORIDA ORE

MATERIAL	RADIUM – 226 (pCi/gm)
INPUT FEED ORE	60
COKE	1
GRAVEL	0.5
OUTPUT ELEMENTAL PHOSPHORUS	
SLAG	58
FERROPHOSPHORUS (FEP)	1.2

Table 11 shows that the other major furnace products, elemental phosphorus and ferrophosphorus contain very small concentrations of radium-226 and since the production quantities of these materials are small in comparison to slag, they account for only a very small fraction of the total radium-226 in the products.

TABLE 11

RADIUM-226 CONCENTRATION IN ELEMENTAL PHOSPHORUS PLANT RAW MATERIALS, PRODUCTS, AND BYPRODUCTS

ONE PLANT USING A BLEND OF TENNESSEE AND FLORIDA ORES

MATERIAL	RADIUM – 226 (pCi/GRAM)
INPUT TENNESSEE MATRIX	3.6
FLORIDA PEBBLE	65.2
COKE	0.28
SILICA	0.36
ELEMENTAL PHOSPHORUS	0.63
SLAG	17.8
FERROPHOSPHORUS (FEP)	0.24
PHOSPHORIC ACID MADE FROM SLUDGE	440 pCi/LITER
PHOSPHORIC ACID MADE FROM CLEAN PHOSPHORUS	101 pCi/LITER

The plant using the blend of Florida and Tennessee rock produced two types of phosphoric acid, one from burning clean acid and another from burning sludge. Analysis of these samples showed that the phosphoric acid made from sludge contained 440 pCi/liter radium-226. Although this is not particularly high, its presence is probably due to the radium-226

present in furnace particulates which were not removed by the furnace precipitator and consequently were scrubbed and collected in the sludge which was then burned to produce acid. It is the existence of particulates missed by the precipitator that causes the sludge material. The acid made from the clean phosphorus contained 101 pCi/liter radium-226. This is probably due to the introduction of radium-226 from the sludge acid since the "clean" acid was composed of 16% sludge acid. Uranium and thorium analyses of these samples have not yet been completed.

No estimates of total activities of radioactivity in elemental phosphorus products and by-products were made because the elemental phosphorus production from Florida rock is only a minor fraction of the total U. S. production. The bulk of this production comes from the use of Western rock. Although field studies have been initiated to examine the concentrations in products and by-products using Western rock, they are presently incomplete.

POTENTIAL URANIUM RESOURCE

The radioactive constituents of the phosphate mining and manufacturing products and wastes have the potential for becoming environmental pollutants. However, the uranium also has the potential for becoming an energy resource if concentrated from phosphate materials and used to fuel nuclear power reactors. Table 12 compares the tons of ore extracted from the earth between the U.~S. uranium and phosphate industries in 1973 and the estimated amounts of uranium and radium-226 contained in the ores. The phosphate industry extracted about 20 times as much rock than did the uranium industry. The uranium industry processed ore averaging about 0.2 percent uranium oxide (U_3O_8), whereas the uranium content of phosphate rock averages about 0.014 per cent uranium oxide (U_3O_8). The Atomic Energy Commission (now Energy Research and Development Administration) reported that in 1973 the uranium industry extracted 13.8 thousand tons of U_3O_8. During that same period, the U_3O_8 content in Florida and Western mined phosphate rock was 18.9 thousand tons. The uranium (U_3O_8) in the marketable phosphate rock fraction was 6.2 thousand tons. Clearly, a substantial amount of uranium comparable to that extracted by the U. S. uranium industry is mined annually by the phosphate industry. Presently, the only technology being developed to recover uranium from phosphate rock is the use of solvent extraction methods to remove the uranium from phosphoric acid. While use of this technology should enable recovery of several million tons of U_3O_8 per year, the bulk of the uranium (about 70%) in the mined rock will still be lost as a resource in the slime fraction and enter the

TABLE 12
COMPARISON OF QUANTITIES OF URANIUM AND RADIUM-226 EXTRACTED BY THE U.S. URANIUM AND PHOSPHATE MINING INDUSTRIES (1973 PRODUCTION DATA)

INDUSTRY		TONS OF ORE (x 10^6)	TONS OF U_3O_8 (x 10^3)	CURIES OF RADIUM - 226
URANIUM MINING INDUSTRY		6.77	13.8	3850[a]
PHOSPHATE MINING INDUSTRY	MINE ROCK	139.7	18.9[b][c]	4900[a]
	MARKETABLE ORE	42.1	6.2[c]	1600[c]

(a) Assuming equilibrium with uranium parent
(b) Assuming 120 ppm uranium in equilibrium with radium - 226
(c) No contribution was included for Tennessee ore and Western rock was also assumed to contain 120 ppm uranium.

environment as a potential pollutant. In addition to the uranium resources lost in the slimes, a substantial resource is also lost by not recovering the uranium in the leach zone that comprises a portion of the overburden in many of the Florida phosphate areas. The leach zone also contains substantial concentrations of uranium (14).

SUMMARY AND CONCLUSIONS

The mining and milling of phosphate rock annually extracts several thousand curies of radium-226, uranium, and thorium-230. Approximately 60% of the activity extracted in mining phosphate rock in Florida remains as waste products of slime and sand tailings after beneficiation. Where mined rock is used directly, the entire amount of radioactivty present in the rock is transferred either to the electric furnace or wet-process phosphoric acid plant. The radioactivity present in the mine rock, marketable rock, slimes, and sand tailings exhibit equilibrium among members of the same decay series.

The slimes contain most of the waste product after beneficiation. Consequently, care must be taken to prevent unnecessary release of slime material to streams and rivers either as suspended solids during normal operations or through accidental slime releases. Studies at operating mine and beneficiation facilities indicate that routine releases of radium-226 from slime ponds can easily be minimized by utilizing good solids setting techniques.

Milling either by electric furnace or the wet-process phosphoric acid process significantly alters the concentration of radium-226, uranium and thorium in the resultant process streams, products and wastes. In the wet-process system, most of the radium-226 is not dissolved by acidilation with sulfuric acid and thus remains with the phosphogypsum by-product. Whereas, most of the uranium and much of the thorium does enter solution and is transferred to the phosphoric acid product. The phosphate products reflect radium-226, uranium, and thorium

concentrations characteristic of the phosphate material from which they were derived. Where phosphoric acid is used as the sole source of phosphorus, the products exhibit relatively low radium-226 concentrations and substantially higher uranium and thorium concentrations. Where both phosphate rock and phosphoric acid are used, the products exhibit both higher radium-226 concentration characteristics of the phosphate rock, and higher uranium and thorium concentrations characteristic of phosphoric acid. In the electric furnace, almost all of the radium-226 is retained by the calcium silicate slag by-product with very little entering the other products. This concentration in the slag may not be true for other radionuclides such as polonium-210, that may be volitalized in the furnace.

Lime neutralization of wet-process effluents was observed to be highly efficient in removing radium-226, uranium and thorium-230. Removal rates of 94% or more for radium-226, uranium and thorium-230 were observed when pH was increased to 6 or more in the field and even at lower pH in the laboratory. Therefore, a properly operated liming system should be capable of minimizing radioactivity levels in wet-process facility effluent streams.

Since a large fraction of the radioactivity that enters either the electric furnace plant or the wet process facility is entrained in the by-product slag and gypsum, respectively, increased emphasis on assessing the potential impact of these materials is warranted. Existing as well as potential future application of these materials such as soil additives, aggregates, gravel and wallboard applications should be

thoroughly investigated to estimate the magnitude of their radiological significance.

The radioactivity concentrations in raw materials, products, wastes, by products and effluents as detailed in the paper should enable individual phosphate processors to estimate the concentrations of radioactivity in their materials. Since individual processors produce varying amounts of specific products, by-products, wastes, and effluents, adaptation of this data to their own specific cases will allow them to better characterize the redistribution of radioactivity in their operations.

This paper is not intended to draw overall conclusions concerning the environmental and public health significance of the data presented. Rather, the existence of this data will enable additional work to model the migration of the radioactivity through the environment to man via the various pathways available and use these models to estimate the individual and overall population impact.

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☆ U.S. GOVERNMENT PRINTING OFFICE: 1975— 632-856/39